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Possible environmental risks of photocatalysis used for water and air depollution – case of phosgene generation

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Abstract

This short review presents some deficiencies regarding photocatalysis used for water and air depollution, because the environmental risks have to be considered in order to minimize negative effects of the future applications. Since photocatalysis was discovered a couple of decades ago, it was intensively studied and many applications were developed. In the environmental engineering depollution ex-situ and in-situ of water and air, using photocatalysis, seems to be revolutionary. Deficiencies of these processes are concerning in formation of undesirable secondary products. Some of the processes involving photocatalysis could degrade efficient by-products, but there are situations when these products seem to be more toxic than initially pollutant. One of these cases, phosgene generation during air depollution, is detailed in a scenario, using related researches and simple calculus. The result proves the environmental risk of organochlorine compounds oxidation by photocatalytic processes.

Keywords: air depollution; environmental risks; photocatalysis; secondary products; water depollution

1. Introduction

Photocatalysis is an advanced oxidative process based on formation of high reactive species at the interface of a semiconductor, when this is irradiated with EM-energy, especially UV and visible light.

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Electrons in solids are situated on energy bands. An occupied band and an unoccupied one are separated by a band gap. In semiconductors, the width of the band gap is lower comparing with band gap in electrical insulators but larger comparing with metals. If a photon from UV or visible range of electromagnetic spectrum is absorbed, an electron (e^-) could be promoted from the valence band (VB) into the conduction band (CB), subsequent generating a hole in the valence band. The resulting electron is a reducing agent, while the hole is an oxidizing one. In the mechanism of the photocatalytic process, the hole can react with water to generate the hydroxyl radical and the electron can reduce molecular oxygen, hydrogen peroxide or some other oxidizing agent in the solution. These conduce to appearance of reactive radicals which are responsible for the removal of hazardous components from the water and air [1 – 6].

In water depollution some medicines, solvents and dyes represent problems. Diclofenac is the disseminated medicine in water, potentially toxic for aquatic life and photocatalysis degraded it successfully; some of secondary products resulted are toxic, even more poisonous as primary pollutant. Degradation of 4-clorophenol under microwave energy couplet with photocatalysis in aqueous solutions occurs with formation of chlorobenzene, phenol, hydroquinone, benzoquinone and 4-chlorocatechol which are undesirable products. Textile dye Acid Red 88 was degraded by sonolysis and photocatalysis, but some intermediate products were not mineralized. The same problem occurred on degradation of diphenylamine from polluted water.

Regarding air depollution, photocatalysis was applying in nasty smells removal; 2-butanone and methyl-ethyl-ketone were successfully oxidized, but acetaldehyde results as secondary product. A pulse discharge system combined with photocatalysis degraded phenols and the problem of sub products appears once again. Some insecticides as malathion, isomalathion and malaoxon were decomposed by photolysis coupled with photocatalysis and some undesirable secondary products formed. Also, trichoroethylene was decomposed successfully by photocatalysis, but it results phosgene, chloroform and carbon tetrachloride.

All the methods need improvement and future researches will find those materials and chemical reactions which have to be eco-friendly.

2. Case studies presentation

2.1. Water depollution

Hai-Chao Liang et al. from Hong Kong, China studied the comparative homogeneous and heterogeneous degradations of diphenamid (DPA) in aqueous solution by photolysis and photocatalysis [7]. Direct photolysis performed with UVC (254 nm) and photocatalysis with TiO_2/UVA (350 nm). Direct homogeneous photolysis was efficient in degradation of DPA up to 100% after 360 minutes, but was not very efficient to mineralize the secondary products (only 8%). In contrast, photocatalysis evolved slowly (only 51% after 360 minutes), but permitted a degradation of byproducts in a higher percent (11%). Analysis identified over 20 intermediates. The mechanism of reactions is quite similar in those two processes, for example as regard oxidation of N-methyl group of molecular chains. Opposite, hydroxylation of aromatic ring was faster in photocatalytic process.

The degradation of 4-chlorophenol (4CP) by a simultaneous microwave assisted UV electrodeless discharge lamp photocatalysis technique (MW/UV/TiO2) was investigated by a Chinese collective [8]. The process is affected by factors like the dosage of photocatalysts, the initial pH value of the solutions, gas bubbling, light intensity and addition of H_2O_2 oxidant. The mechanism proposed is a pseudo-first-order one relative to 4CP degradation. Synergistic effects between microwaves and photocatalysis were observed too. Intermediates found were chlorobenzene, phenol, hydroquinone, benzoquinone and 4-chlorocatechol. All of these are dangerous for human health, if they are not properly controlled. The photodegradation of 4CP involved stages, as follow: (a) direct photolysis by UV light; (b) hydroxylation of the aromatic ring; (c)

substitution of chlorine by *OH; (d) oxidation of chlorinated hydroquinone to quinine; (e) oxidation to aliphatic intermediates; (f) mineralization to carbon dioxide and water. Of course, in ideal situation, mineralization would be total and undesirable byproducts are quantitatively quite zero, an aim for next technologies.

Degradation of Acid Red 88 by combined sonolytic and photocatalytic action was studied by Madhavan et al. from Australia, India [9]. Acid Red 88 (AR88) is a mono-azo dye used in the textile and food industries like colorant. Sonolytic, photocatalytic and sonophotocatalytic decomposition of AR88 was performed in the presence of Fe^{3+} and TiO_2 as photocatalyst. The effects of initial concentration of dye and of ultrasound power were investigated and a first order-like kinetics was established. A synergetic effect was observed, so sonolysis combined with photocatalysis was the efficient process. Mineralization was studied analyzing total organic carbon (TOC) and sonophotocatalysis method exhibits better results. As byproducts mono and di-hydroxylated compounds were identified using electrospray mass spectrometry (ESMS). Also a degradation pathway was proposed. As an interesting fact to be signalized, byproducts appeared in all studied processes (sonolysis, photocatalysis and sonophotocatalysis).

L. Rizzo et al. (Napoli, Italy and Nicosia, Cyprus) focused their studies on degradation kinetics and mineralization of diclofenac (DCF) by TiO_2 photocatalysis [10]. Like control tell-tale a set of bioassays (Daphnia magna, Pseudokirchneriella subcapitata and Artemia salina) was used to evaluate DCF toxicity and obviously, degradation of DCF. The kinetic of reactions seems to be a pseudo-first-order one. Some secondary products formed were more toxic than DCF. Best results were achieved for low concentrations of DFC, so the process could be very efficient for post-treatment of wastewaters. The first two species noted as above were sensible at DFC and different conditions of experiment, while the third (Artemia salina) proved to be not sensitive under the investigated conditions. UV absorbance could be also a fast indicator for preliminary results as concern organic intermediates formation.

2.2. Air depollution

The reduction of nasty smells by photocatalytic oxidation was studied by G. Vincent and O. Zahraa from Nancy Cedex, France [11]. 2-butanone and methyl-ethyl-ketone (MEK) were considered like volatile organic compounds with moderated molecular mass (< 100 g/mol) because these could cause a serious olfactory discomfort. The photocatalytic degradation occurred on commercial TiO_2 Degussa P25 deposited on glass fibers. The compounds were disintegrated successfully, but as a secondary product acetaldehyde was formed. It is known that acetaldehyde is undesirable because has a cancerous potential. Also a mechanism of chemical reaction was proposed, following Langmuir-Hinshelwood kinetics. This mechanism wants to be able to predict other secondary products which could appear in the photochemical reactions and to point the path for diminished the undesirable byproducts.

M. Bavcon Kralj et al., Slovenia pointed to degradation by photo-catalysis of some toxic compounds (malathion, radothion, isomalathion, malaoxon – frequently used as insecticides in agriculture) [12]. Gas-chromatography for analyses was used. Positive results achieved have to be enhanced because some toxic byproducts were formed. For toxicity studies the enzyme ASChI (acetylthiocholine iodide) was the control tell-tale.

Madjid Mohseni, Vancouver, Canada, studied photo-oxidation of trichloroethylene (TCE) by photocatalysis with TiO_2 and photolysis [13]. Ultraviolet illumination was provided by lamps with outputs of 254 nm, 365 nm and 185/254 nm wave length. Even the results were satisfactory, especially when coupled system was used, undesirable byproducts as phosgene, chloroform, carbon tetrachloride and dychloro-acetyle chloride (DCAC) were produced too. Figure 1 presents time evolution for TCE, DCAC and phosgene concentration.

Another study regarding photocatalysis of trichloroethylene (TCE) under TiO_2 was realized by Hsing-Hung Ou et al. (Taiwan). They investigated the effects of the oxygen and relative humidity (RH) on the formation of the dichloroacetyl chloride (DCAC) and phosgene [14]. Because the reaction rate constants of TCE are almost one order larger than that of DCAC, it results an accumulation of by-product. For optimal conditions (oxygen and RH) this could be diminished. Phosgene also is formed like a secondary product, but it seems to be generated from DCAC degradation more than from TCE destruction. An elevate level of oxygen conduced to phosgene inhibition.

3. Results and discussions

From the presented data it could be signalized that secondary products of the reactions could not be avoided. Taking as examples the last two related articles [13,14] it will be discussed the situation of phosgene generation.

Phosgene concentration values exceeds maximum admissible limit during TCE degradation [8]. A similar result is proved by Madhavan et al. [9]. Even the TCE degradation is quite complete, phosgene concentration exceeds 20 times the limits. For these reasons, a photocatalytic degradation of TCE could be performed only in closed area reactors, for in-situ depollution applications (in industry).

Phosgene (CCl_2O) is a colourless gas used like reagent in chemical industry and synthesis of pharmaceuticals. Its odour brings to mind freshly cut grass or hay. Molar mass of phosgene is 98.92 g/mol. Phosgene could be generated by industrial production, but it could appear also from combustion of organochlorine compounds. During the First World War, phosgene was used like combat toxic gas, a fact that emphasizes them dangerous potential [15]. The maximum admissible limit in the ambient atmosphere is 0.02 ppm for 8 hours (or 0.08 mg/m^3) and 0.1 ppm for 15 minutes (0.4 mg/m^3) [16].

Dichloracetyl chloride (DCAC, having compressed chemical formula C_2Cl_3HO), is a chlorinated hydrocarbon with molar mass 147.39, used mainly like organic solvent [17]. Maximum admissible limits are 3 mg/m^3 for 8 hours and 5 mg/m^3 for a short time (15 minutes) exposure.

Trichloroethylene (TCE, with formula C_2HCl_3), a chlorinated hydrocarbon is known also like trichloroethene (the IUPAC name), and it is used like solvent. Molar mass of TCE is 131.39 g/mol. Maximum acceptable limits for TCE are 100 mg/m^3 for 8 hours, 150 mg/m^3 for 15 min respectively, in atmospheric air. But TCE could pollute also the groundwater.

A comparison of maximum acceptable limits between phosgene and TCE is interesting for a scenario. For this purpose, data available from public sources were compiled. A simple ratio (data for 15 minutes exposure) discloses that if we have a half maximum concentration of TCE (75 mg/m^3), that means 0.57 mol/m^3 and secondary product phosgene is generated at 1% molar ratio, the result gives 0.56 g/m^3 phosgene, a value higher than maximum admissible limit. Supposing the same value for TCE and the same percent (1%) for transformation in DCAC, after calculus a value of 0.84 mg/m^3 was achieved. This value do not exceed maximum acceptable limit, comparing with phosgene generation case.

4. Conclusions

Even photocatalytic processes seem to be revolutionary, there are aspects to be clarified and one of this is represented by secondary undesirable products which appear in photochemical reactions. The mechanism of photochemical reactions is complicated and further studies have to establish the path to achieve complete mineralization or even diminishing of these compounds, to allow large scale industrial and commercial applications. Many times there are secondary unknown products, in sense of unpredictable, so the research

has to find them, to prevent environmental negative effects. Phosgene generation during oxidation of organochlorine compounds represents a risk.

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